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Synthesis, Spectroscopic Characterization and Biological Studies for New Binuclear Schiff Base with Some Transition Metal

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Abstract
A new series of transition metal complexes of Co (II), Ni(II), Hg(II), Cu(II) and Mn(II) have been preparaed of the binuclearing schiff base (H_2L) derived from benzidine and gloxylic acid have been synthesized and characterized by means of various elemental analysis,conductivity measurements,magnetic moment, NMR, IR and electronic spectral studies. The ten complexes have been taken in two stoichiometries of 1:1 and 1:2 (M:L), where in azomethine nitrogen and carboxlic oxygen of ligand is coordinated to metal. From the obtained data the octahedral geometry was suggested for prepared $[(CoL)_2(H_2O)_4]$, $[(NiL)_2(H_2O)_4]$, $[(CuL)_2(H_2O)_4]$ and $[(MnL)_2(H_2O)_2]$ complexes also $[(NiCl)_2(L)(H_2O)_2]$,$[(CuCl)_2(L)(H_2O)_2]$,$[(HgCl)_2(L)(H_2O)_2]$and $[(HgL)_2]$ complexes have been square planar geometry while $[(MnCl)_2(L)(H_2O)_2]$ and $[(CoCl)_2(L)(H_2O)_2]$ complexes have been tetrahedral geometry.In addition biological activity of the ligand and it's complexes tested against four selected type of bacteria were used includes *Bacillus, Escherichia Coli*, *Pseudomonas* and *Staphylococcus aureus*.All the complexes exhibit good bacterial activities.
Keywords: new schiff base, benzidine, transition metal complexes, and biological activity.

I Introduction

The metal complexes of schiff bases play an important role in the development of coordination chemistry, resulting in an enormous number of publications, ranging from pure synthetic work to physicochemical [1] and biochemical relevant studies of metal complexes and found wide range of applications [2-6]. The spectroscopic characterization of some tetra dentate schiff bases and their complexes with nickel, copper and zinc has been studied by Mokhles M. Abd-Elzaher [7]. The class of schiff bases derived from an amine and any aldehyde are compounds which co-ordinate to metal ions via the azomethine nitrogen [8]. Because of the variety of ways in which they are bonded to metal ions chelating ligands containing O and N donor atoms show broad biological activity [13]. It is well known that several Schiff base complexes have anti-inflammatory, antipyretic, analgesic, anti-diabetic, anti-bacterial, anti-cancer and anti-HIV activity [14, 15].

The N_2O_2 donor of schiff base complexes form different ligands complexes which often combine with other metals of same different types through their O,O donors, thereby acting as precursors for new poly nuclear homo-/ hetero-metallic complexes leading to rich coordination chemistry[16]. The interesting in N_2O_2 type ligands were increasing in the last decades is related to the is wide range of biological properties, for example as antiviral, anti-bacterial and anticancer agents [17-21].These biological activities are often attributed to their chelating ability with metal ions copper complexes of bis (N_2O_2 type ligands) have been investigated for use as anticancer chemotherapeutic agents [22,26] ,some zinc complexes that have been shown to be active as anti-tumor agents are as cytotoxic as cis-platin and are also effective against cisplatin-resistant cell lines [27].

Benzidine used in as an amination reactant for synthetic of the schiff base.It was predictable that interaction of carbonyl compounds with benzidine would proceed with participation of both amino groups, resulting in cross linking of two molecules of substrate[23,24]. An important role in stereo controlled the syntheses of various organic compounds of derivatives of glyoxylic acid and its simple analogs, such as pyruvic or phenylglyoxylic acid, readily available via reactions with chiral alcohols or amines.These compounds allow for easy introduction of hetero functionalities, often met in natural products and their analogs[25,26]. The binuclear transition metal complexes have been an interest for many years were schiff base ligands because of the relation between structures and magnetic exchange effects in homo- and hetero-binuclear metal complexes [27- 28] which are play an important role in developing the coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures [29]. Because of their ability to possess unusual configuration, being structurally labile and their sensitivity to molecular environment transition metal complexes with oxygen and nitrogen donor schiff base ligands are of particular interest [30-35]. Additionally, these complexes have wide applications such as antibacterial and antifungal agents [36].

In this paper the synthesis of new tetra dentate N_2O_2 donor type schiff base derived by the condensation benzidine and glyoxalic acid. And the transition metal complexes preapered from this schiff base with hydrated Cu(II),Ni(II),Mn(II),Co(II) and Hg(II)chlorides in1:1 or 1: 2 molar ratio. These complexes were binuclear complexes expected to have high biological activity.

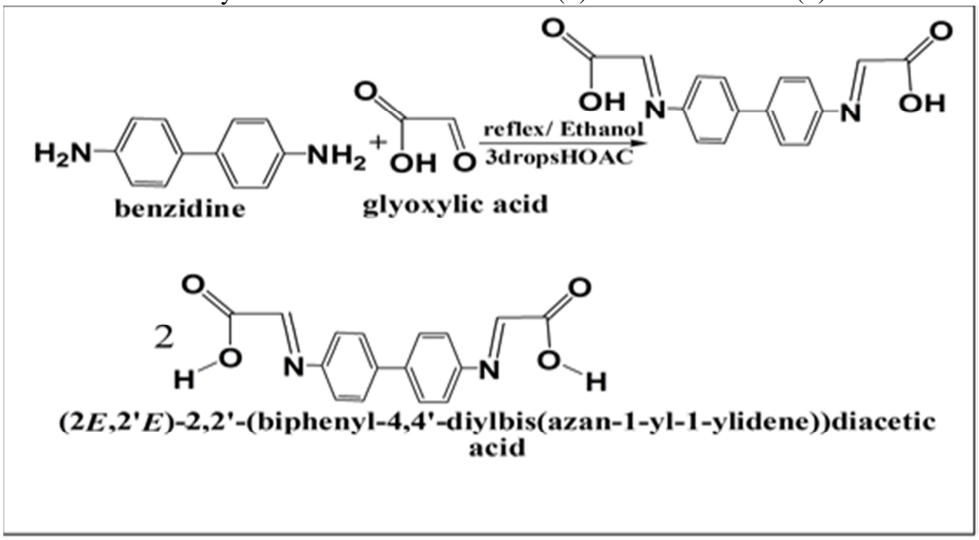
II. Experimental

Materials and Methods: All chemicals used for the prepared were of reagent grade. Benzidine (Fluka,Germany), glyoxylic acid from sigma Chemical Co.(USA), all reagent and solvents like DMSO (Merck) and Ethanol (commercial) and glacial acetic acid (Merck) were of high purity and were used without further purification[16].The metal salts used for complexation: Cobalt (II) chloride hexahydrate ; Copper(II) chloride dihydrate; Manganese (II) chloride tetrahydrate ;Nickel(II) chloride hexahydrate ; and Mercury (II) chloride were obtained from British Drug House (BDH) Chemical Limited Company. The compounds purity was determined by thin layer chromatography (TLC) or dry column "flash" chromatography (DCFC) (SiO_2, Merck Kieselgel 60 -H).

Measurements: Products were examined by FT-IR spectra were recorded on SHIMADZU FTIR–8400 Fourier Transform Infrared spectrophotometer as KBr disc.^{1}HNMR and ^{13}C NMR spectra were recorded on Bruker specrospin ultra shield magnets 300 MHz instrument using tetramethyl silane (TMS) as an internal standared and DMSO-d_6 as a solvent in Ahl-Albate University in Jordan. The chlorid content determined using potentiometric titration method on 686 -Titro Processor -665 Dosim A- Metrohm /Swiss. Magnetic susceptibility measurements were obtained at room temperuture on the solid state applying Faraday's Method using Bruker BM6 instrument. Melting points were determined in Gallen Kamp melting point apparatus and were uncorrected. Antibacterial screening was done at central laboratory in biological department, college of science, university of Baghdad, using agar diffusion technique.

Preparation of schiff base

The schiff base was prepared from the reaction of (0.148g, 2moles) glyoxlic acid, with benzidine (0.184,1mole), in 25ml ethanol absolute and (3-4) drops of glacial acetic acid.This mixture was refluxed on water bath at (70°C) during 4-5hrs. A product mass separated out on cooling, was filtered off.A yellow Precepitate was obtained then rercystallized from a hot mixture of [(5ml) methanol,(5ml) acetone and (2ml) distilled water].[10] The ligand H_2L that is formed from the [2+1] condensation. This product was furthermore subjected to dry column "flash" chromatography (DCFC) using ethanol as eluent, and its yield was almost quantitative (87%), melting point (233) °C, and elemental microanalysis C.H.N were listed in Table(1) and showed schem(1) .



Scheme(1)Synthetic route of the Schiff base ligand H_2L

Preparation of Mn(II), Ni(II), Co(II), Cu(II) and Hg(II)complexes.

All the complexes were prepared using the same synthetic pathway described in literature [26- 28] by mixing in(15mL) absolute ethanol of ligand H_2L (0.3 g, 1mmol L^{-1}) and hydrated cobalt(II),copper(II), Mercury (II), Manganese(II) and nickel(II) chlorides in 1 : 1 or 1 : 2 molar ratio. After stirring at 50°C for(30 min.) The precipitate immediately formed, filtered off, washed several times and recrestallized from a hot of (10mL) ethanol . Their purity was verified using thin layer chromatography (TLC) and ethanol / CH_2Cl_2 (3:7, v/v) as eluent and were shown, in any case, to contain only one component (R_f0.55). These products were again subjected to (DCFC) to afford the 1 :1or 1 : 2-complexes in yields (93–79%) (Table1).

III Results and Discussion:

The binuclearing Schiff base [2E,2'E)- 2,2'- (biphenyl- 4,4'-diylbis (azan-1 -yl -1- ylidene))diacetic acid] was synthesized by the condensation reaction of benzidine and glyoxylic acid in one step according to Scheme(1).The preapered Schiff base H_2L was tetradentate ligand to form the ten complexes reported in this work. This ligand employs two oxygen atoms and two imine nitrogen to bind the metals. The (ligand- metal) ratio is compatible with the 1: 2 or 1 : 1 form depending on the molar ratio of the mixed reactants used in the

preparation.

The observed molar conductance of all complexes in lie in the range(58.6-113.65) $S.cm^2.mol^{-1}$, in(10^{-3}M) water solutions indicating non-electrolyte behavior[24,25]. Analytically pure solid compounds were get in all cases as indicated by elemental analysis are given inTable(1).They are of higher melting points than the free ligand (can be taken as a guide for the bonding to the copper(II) ,cobalt(II), Mercury (II), nickel(II) or Manganese(II) ions with chelate rings formation [28]

Infrared Spectra of the Ligand and the Complexes.

The IR stretching frequencies for the Schiff base (H_2L) and it's complexes are listed in Table(2). The formation of Schiff base ligand is deduced by the appearance of a strong bond in the IR spectrum at (1678) cm^{-1},which was due to(C=N)imine group. Anther stretching frequency of O-H group of the Schiff base ligand exhibited board band at(3352 cm^{-1}), which were due to stretching frequency of O-H group. The IR data are presented in the Table(2) Comparison of the IR spectra of the Schiff base ligand with that of its complexes showed the absorption bands in the range (1636-1660) cm^{-1} due to azomethine (C=N) groups.The (C=N) vibrations decreased on complexation showing involvement of nitrogen of azomethine group in coordination[23]. The free ligand (H_2L) exhibits two absorption bonds at (1631)cm^{-1} and (1462) cm^{-1} due to the stretching vibration of due to $\upsilon_{asymm}(COO^-)$ and $\upsilon_{symm}(COO^-)$of carboxylic group. These band are shifted slightly to lower frequency to two bands, one band in rang (1528-1558)cm^{-1} due to $\upsilon_{asymm}(COO^-)$ and another band due to $\upsilon_{symm}(COO^-)$ in rang(1327-1311)$cm^{-1}$and $\Delta\upsilon = \upsilon_{asymm}(COO^-) - \upsilon_{symm}(COO^-)$ in rang (235- 204) cm^{-1}upon complexation. The values of ($\Delta\upsilon$) for all complexes refer to the carboxylate group behaves as tetradentate group.

The band broad bands at (3396-3315)cm^{-1} are due to υ(OH) hydraded water, and new bands are found in the spectra of the complexes in the regions (964-941)cm^{-1}attributed to $\delta(H_2O)$ coordinate water[12]. On complexation, it is well strategy to compare the spectra of the free ligand and its complex to account for the chelation site(s).New bands were emerged for the complexes which were not seen in the free ligand, these bands were assigned for M-O and M-N. These bands at rang (594-570) cm^{-1} which are assigned to υ (M-O) mode[18].The other bands at (482- 465)cm^{-1} have been assigned to υ(M- N)mode[19]. And showed some another bands due to ($C=C_{aromatic}$) are listed in Table(2). Therefore from IR spectra, it is concluded that the ligand behave as tetradentate and bind to the metal ions via the two imine N and two carboxylate O.

NMR spectrum for the ligand (H_2L)

^{1}H-NMR spectrum of the ligand (H_2L)in DMSO–d_6 Table(2), Fig.(5) is characterized by the appearance of chemical shift related to The proton of the protons aromatic at (7.96-5.45) ppm.The characteristic signals at (8.06)ppm. is assigned to HC=N. The COOH signals is found at (9.98-10.86)ppm. .The DMSO signal appeared at (2.50) ppm.[13].

^{13}C–NMR of the free ligand(H_2L)Table (3)Fig(6)shows the HC=N peak at (123.45) ppm., the COOH peak at (159.83)ppm, and carbon peaks for aromatic are detected at (112.5-118.41) ppm.The peak at (40.25) ppm. assigned to DMSO [7-8].

The electronic absorption spectral and magnetic studies

The most detailed information provided by UV-Vis spectra about the electronic structure. The UV-Vis spectrum of the complexes, the band at 268 nm(37312cm^{-1})remains as such, in agreement with the $\pi \rightarrow \pi^*$ transition of the schiff base ligand. The band observed at 322 nm(31055cm^{-1}) observed in the spectrum of the free ligand (H_2L) is red shifted in rang (334-342) nm in complexes in the form of ligand to metal charge transfer transition(LMCT).

The U.V-Vis spectrum of the binuclear $[(CoCl)_2(L)(H_2O)_2]$ complex showed one weak band was from d-d transition was observed at (627)nm(15948 cm^{-1}) which may be assigned to $^4A_2g_{(F)} \rightarrow {}^4T_1g_{(F)}$ correspond to a tetrahedral Environment around the of Co^{2+} ion. The magnetic moment of Co(II) complex was found to be 5.12 B.M. which is at the lower end magnetic moments expected for tetrahedral Co(II) complex suggest the dimeric nature of the complex [16]. While the electronic spectrum of the $[(Co)_2(L)_2(H_2O)_4]$complex displayed two peaks at (407)nm (24570 cm^{-1}) and (846)nm (12240 cm^{-1}) were attibuted to (d-d) electronic trasitions type $^4T_1g_{(F)} \rightarrow {}^4T_1g_{(P)}$ and $^4T_1g_{(F)} \rightarrow {}^4T_2g_{(F)}$ respectively, suggesting high spin octahedral geometry around Co(II) central ion [20]. The magnetic moment Co(II) complex is (5.67) B.M. also it is indicative of four unpaired electron per Co(II)ion suggesting consistency with its octahedral environment[21].

The U.V-Vis spectrum of the binuclear $[(NiCl)_2(L)(H_2O)_2]$complex displayed two bands at (448) nm(22321 cm^{-1}) and (613) nm(16313 cm^{-1}) that may be assigned to the $^1A_1g \rightarrow {}^1B_1g$ and $^1A_1g \rightarrow {}^1A_2g$ transitions, indicating a square planar environment around the nickel(II) metal ions [13] may be confirmed by the diamagnetic properties of the complexes.While the electronic spectrum of the$[(NiCl)_2(L)(H_2O)_2]$complex showed two peaks at(625)nm (16000cm^{-1}) and (892) nm (11210cm^{-1}), Table (5) were attributed to (d-d) electronic transtion type $^3A_2g_{(F)} \rightarrow {}^3T_1g_{(P)}$ and $^3A_2g_{(F)} \rightarrow {}^3T_1g_{(F)}$ respectively, that is agood suggestment with high spin octahedral geometry [22]. The magnetic susceptibility measurement for the solid Ni(II) complex is (3.16) B.M. also is

indicative of two unpaired electron per Ni (II) ion suggesting consistency with its octahedral geometry[23].

The U.V-Vis spectrum of the binuclear $[(MnCl)_2(L)(H_2O)_2]$ showed two weak bands from d-d transitions were observed at (409)nm (24449 cm^{-1})and 541 nm(18484 cm^{-1}), which may be assigned to $^6A_1 \rightarrow {}^4A_{1(G)}$ and $^6A_1 \rightarrow {}^4E_{(G)}$, respectively are characteristic of four coordinated tetrahedral Mn(II) complex [15]. Magnetic moment of manganese(II)complex is 5.56 B.M. which suggest that the complex is four coordinated.While the U.V-Vis spectrum of the$[(Mn)_2(L)_2(H_2O)_4]$ showed two weak bands from d-d transitions were observed at (404) nm(12610 cm^{-1}) and (557)nm (17953 cm^{-1}),which may be assigned to $^6A_1g \rightarrow {}^4Eg_{(D)}$,$^6A_1g_{(S)} \rightarrow {}^4T_2g_{(G)}$,respectively are characteristic of six octahedral Mn(II) complex[16]. The magnetic moment of manganese(II)complex is 5.72 B.M. which suggest that the complex is six–coordinatedTable(5),which suggests the presence of one unpaired electron with its octahedral environment[26].

The absorption spectrum of $[(CuCl)_2(L)(H_2O)_2]$ complex show a broad band at about 590 nm (16949 cm^{-1}) was attributed to $^2B_1g \rightarrow {}^2A_2g$ transition which is well within the range of (610-555) nm (16393- 18018cm^{-1}) expected for square planar.The magnetic susceptibility measurement for this complex was found to be 1.74 B.M. per Cu(II) ion which was in usual range for square planar copper complexes and indicating no direct interaction between the two copper centers in the solid state at room temperature [12]. While the absorption spectrum of the $[(CuL)_2(H_2O)_4]$ complex exhibited two bands at (462) nm(21645 cm^{-1}) and (755) nm(13245cm^{-1}) were attributed to (d-d) electronic transtion type $^2B_1g_{(F)} \rightarrow {}^2A_1g_{(F)}$,$^2B_1g_{(F)} \rightarrow {}^2A_2g_{(F)}$, that is a good suggestment with high spin octahedral geometry [24].The magnetic susceptibility measurement of Cu(II) complex is (1.79) B.M. ,which suggests the presence of one unpaired electron with its octahedral environment[25].

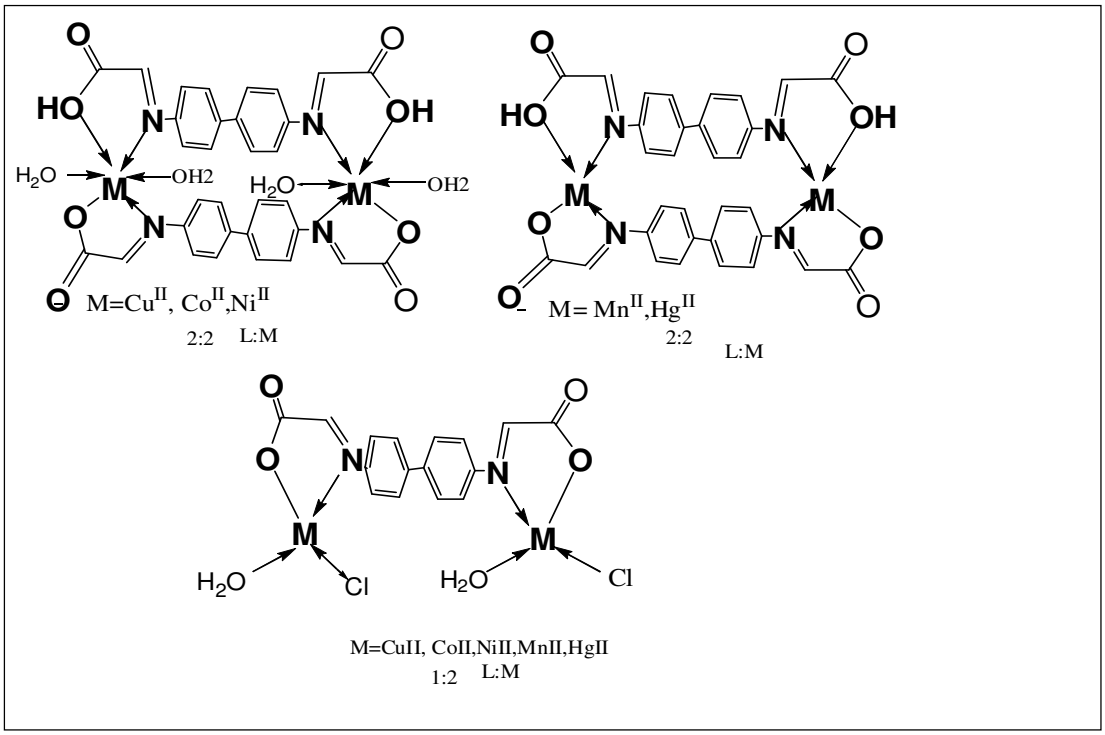
The U.V-Vis spectrum of the$[(HgCl)_2(L)(H_2O)_2]$complex displayed peak (351) nm (28490 cm^{-1}) refer to charge electronic transtion only [27,28]. While the electronic spectrum of the $[(HgL)_2]$complex showed no d-d transitions in the visible region, indicating for While,this is mean electronic transitions happened sqruare planar geometry has been assigned to the Hg(II) complex. From the interpretation of elemental analysis, electronic spectra, infrared, magnetic measurements and molar conductivity, it is possible to draw up the tentative structures of the transition metal complexes. Fig.(5,6)depicts the representative structure of the metal complexes.

Biological Activity

Disc diffusion method was used for screening the ligand and its complexes[9] for primary selection of the compounds as therapeutic agents. The complexes tested against gram(-)*Bacillus, Escherichia Coli*, *Pseudomonas* and gram(+)*Staphylococcus aureus*. Nutrient agar(NA) plates were incubated with H_2O of an appropriate dilution of the tested culture and the sample solutions were loaded on the wells of the bacterial culture incubated at 37°C for 24 hrs. during the period, the test solution diffused and the growth of the inoculated microorganisms was affected.The zone of inhibition was calculated in centimeters[19-21]. The binuclearing Schiff base ligand drived by the condensation of benzidine and glyoxylic acid and it's, Mn(II), Ni(II), Co(II) Cu(II) and Hg(II) complexes showed inhibition diameter against all the type of bacterial, the results indicate that the complexes showed more activity than the ligand under similar experimental conditions. The antimicrobial activities of the prepared ligand and its complexes are given in (Table 6), (Figures.10).The data reveal that all compounds have good biological activity and some complexes have higher activities than the free ligand. As previously reported, the metal salts do not exhibit antimicrobial activity [30].Accordingly, the antimicrobial activity of the ligand and its complexes can be referred to the increase of their lipophilic character which in turn deactivates enzymes responsible for respiratory processes and probably other cellular enzymes, which play a vital role in various metabolic pathways of the tested bacteria. Also it is proposed that the action of the toxicant is the denaturation of one or more proteins of the cell and this impairs normal cellular process[31]. Table (6) Diameter of zone of inhibition.

Conclusion

The new binuclearing shiff ligand(H_2L) shows in scheme (2)and metal complexes were aprepared$[(CoCl)_2(L)(H_2O)_2]$, $[(NiL)_2(H_2O)_4]$, $[(NiCl)_2(L)(H_2O)_2]$, $[(CuL)_2(H_2O)_4]$, $[(CuCl)_2(L)(H_2O)_2]$, $[(MnL)_2(H_2O)_2]$, $(MnCl)_2(L)(H_2O)_2]$, $[(HgCl)_2(L)(H_2O)_2]$ and $[(HgL)_2]$.Spectroscopic,structurical and magnetic data show that $[(CoL)_2\ (H_2O)_4]$, $[(NiL)_2(H_2O)_4]$,$[(CuL)_2(H_2O)_4]$ and $[(MnL)_2(H_2O)_2]$complexes are six-coordinate metal complexes also $[(NiCl)_2(L)(H_2O)_2]$, $[(CuCl)_2(L)(H_2O)_2]$, $[(HgCl)_2(L)(H_2O)_2]$, $[(HgL)_2]$, $[(MnCl)_2(L)(H_2O)_2]$ and $(CoCl)_2(L)(H_2O)_2]$ complexes are four-coordinate owing to the lgation of binuclearing schiff base moieties with four or two coordinated water and two coordinated chloride shows in scheme (2).



Scheme (1) Synthetic route of the complexes

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Table (1):Color,elemental analysis, molarconductivity,solubility,m.p and weight of metal salts of the Schiff base and it's complexes under investigation.

Empirical Formula	Yield%	M.P°C	Colour	Metal salt	Weight(g)mmolL^{-1}	Condscm^{2}mol^{-1}	Calc.)% Found					Solubility
							C	H	N	Cl	Metal	
L=$C_{14}H_{12}N_2O_2$	87	233	yellow	-	-	-	(76.74) 77.50	(5.81) 5.40	(8.13) 8.42	-	-	H_2O,DMSO, DMF
$[(CoCl)_2(L)(H_2O)_4$	78	<260	Dark yellow	$CoCl_2.2H_2O$	0.476	93.7	(76.74) 77.50	(76.74) 77.50	(76.74) 77.50	(12.01) 11.91	(19.97) 19.18	=
$[(CoL)_2(H_2O)_4]$	84	<256	brownish		0.238	72.9	(76.74) 77.50	(76.74) 77.50	(76.74) 77.50	-	(14.98) 14.42	
$_2(L)(H_2O)_4])$ [(NiCl	85	<260	Greenth brown	$NiCl_2.2H_2O$	0.476	108.7	(76.74) 77.50	(76.74) 77.50	(76.74) 77.50	(12.01) 11.88	(19.97) 19.72	=
$[(NiL)_2(H_2O)_4]$	79	<256	brown		0.238	80.8	(76.74) 77.50	(76.74) 77.50	(76.74) 77.50	-	(14.98) 14.35	
$_2(L)(H_2O)_4$][(MnCl	88	244	pale brown	$MnCl_2.2H_2O$	0.396	67.5	(76.74) 77.50	(76.74) 77.50	(76.74) 77.50	(11.83) 11.25	(21.17) 20.82	=
$[(MnL)_2(H_2O)_4]$	83	<256	brown		0.198	58.6	(76.74) 77.50	(76.74) 77.50	(76.74) 77.50	-	(16.14) 15.60	
$_2(L)(H_2O)_4$][(CuCl	78	250	Dark brown	$CuCl_2.4H_2O$	0.34	113.6	(76.74) 77.50	(76.74) 77.50	(76.74) 77.50	(12.18) 11.91	(18.87) 19.13	=
$[(CuL)_2(H_2O)_4]$	88	248	brown		0.170	86.9	(76.74) 77.50	(76.74) 77.50	(76.74) 77.50	-	(14.29) 13.64	
$[(HgCl)_2(L)(H_2O)_4]$	86	<260	Pale brown	$HgCl_2$	0.542	99.6	(76.74) 77.50	(76.74) 77.50	(76.74) 77.50	(8.13) 7.72	(45.82) 45.21	=
$[(HgL)_2(H_2O)_4]$	79	<256	brown		0.271	65.7	(76.74) 77.50	(76.74) 77.50	(76.74) 77.50	-	(37.74) 37.08	

Table (2): H-NMR Chemical Shifts for Ligand (H_2L) (ppm in DMSO)

HC=N	C-H $_{aromatic}$	COOH
δ =3.87ppm	Hδ = 5.85-8.35ppm	δ =10.86ppm

Table (3):^{13}C-NMR Chemical shifts for Ligand (H_2L) (ppm in DMSO)

C-$H_{aromatic}$	HC=N	COOH
δ =123.28-136.56ppm	δ = 147.26ppm	δ = 162.87ppm

Table (4): Infrared spectral data(wave numberυ)cm^{-1}for the ligand (H_2L) and its complexes

Compound	υ(OH)$_{carboxylic}$	υ(HC=N)$_{imine}$	υ(C=O)	Δυ	υ(C=O)	υ(C=C) $_{aromatic}$	υ(OH)$_{coordinate}$	δ(OH)	M–N M–O
H_2L	3352	1678	1533	218	1315	1606	-	-	-
$[(CoCl)_2$ $(L)(H_2O)_2]$	-	1660	1558	235	1323	1589	3354	954	555 437
$[(CoL)_2(H_2O)_4]$	-	1657	1531	218	1313	1602	3331	950	553 433
$[(NiCl_2(L)(H_2O)_2]$	-	1637	1531	220	1311	1602	3321	941	551 447
$[(NiL)_2(H_2O)_4]$	-	1642	1533	219	1314	1604	3315	936	551 437
$[(MnCl$ $)_2(L)(H_2O)_2]$	-	1651	1527	212	1315	1598	33296	943	541 432
$[(MnL)_2(H_2O)_4]$	-	1647	1528	215	1313	1604	3319	964	552 421
$_2(L)(H_2O)_2]$)[(CuCl	-	1640	1535	218	1317	1600	3315	947	555 452
$[(CuL)_2(H_2O)_4]$	-	1636	1538	218	1320	1604	3346	953	553 427
$[(HgCl)_2(L)(H_2O)_2]$	-	1645	1531	204	1327	1602	3338	949	558 453
$[(HgL)$ $_2(H_2O)_4]$	-	1654	1548	230	1318	1603	3325	951	543 462

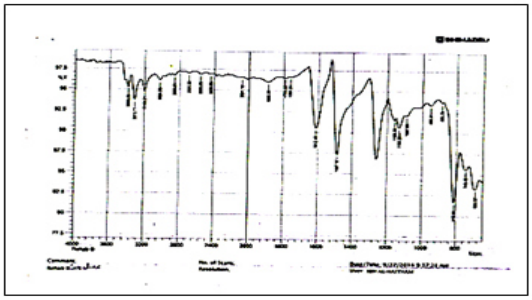
Table (5): Electronic spectral data of the ligand (H_2L) and its metal complexes

Compound	μ_{eff}	λnm	υwave number cm^{-1}	(εmax molar^{-1} cm^{-1}	Assignments	Proposed structure
H_2L	-	268	37313	1348	π→π*	-
		334	29940	2415	n→π*	
$[(CoCl)_2(L)(H_2O)_2]$	5.12	627	15948	32	$^4A_2g_{(F)} \rightarrow {}^4T_1g_{(F)}$	Tetrahedral
$[(CoL)_2(H_2O)_4]$	5.67	407	24570	1293	$^4T_1g_{(F)} \rightarrow {}^4T_1g_{(P)}$	Octahedral
		846	11820	56	$^4T_1g_{(F)} \rightarrow {}^4T_2g_{(F)}$	
$[(NiCl)_2(L)(H_2O)_2]$	dimagnatic	448	22321	1312	$^1A_1g \rightarrow {}^1B_1g$	Square planer
		613	16313	42	$^1A_1g \rightarrow {}^1A_2g$	
$[(NiL)_2(H_2O)_4]$	1.82	625	16000	45	$^3A_1g_{(F)} \rightarrow {}^3T_2g_{(F)}$	Octahedral
		892	11210	21	$^3A_1g_{(F)} \rightarrow {}^3T_2g_{(F)}$	
$_2(L)(H_2O)_2]$)[(MnCl	5.56	409	24449	1193	$^6A_1 \rightarrow {}^4A_{1\,(G)}$	Tetrahedral
		541	18484	1100	$^6A_1 \rightarrow {}^4E_{(G)}$	
$[(MnL)_2(H_2O)_4]$	5.72	442	22624	1098	$^6A_1 \rightarrow {}^3E_2g_{(G)}$	Octahedral
		580	17241	1120	$^6A_1g_{(S)} \rightarrow {}^4T_2g_{(G)}$	Squar planar
$_2(L)(H_2O)_2]$)[(CuCl	1.74	590	16949	33	$^2B_1g_{(F)} \rightarrow {}^2A_2g_{(F)}$	Octahedral
$[(CuL)_2(H_2O)_4]$	1.79	462	21645	1455	$^2B_1g_{(F)} \rightarrow {}^2A_1g_{(F)}$	
		755	13245	53	$^2B_1g_{(F)} \rightarrow {}^2A_2g_{(F)}$	
$[(HgCl)_2(L)(H_2O)_2]$	-	490	20408	1029	Charge transfer	Squar planar
$[(HgL)$ $_2(H_2O)_4]$	-	442	22624	1100	Charge transfer	Squar planar

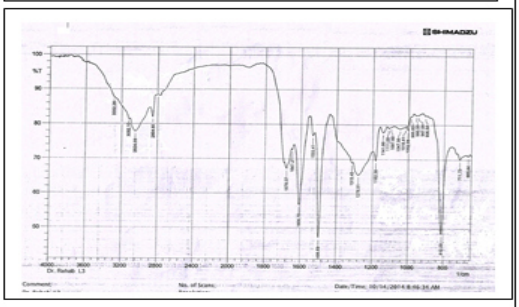
Table(6) Diameter of zone of inhibition (mm)

Comp.	*Escherichia. Coli(G-)*	*Staphylococcusaureu*	*Bacllus*	*psseudmona*
$L=C_{14}H_{12}N_2O_2$	**4**	**2**	**-**	**6**
$[(CoCl)_2(L)(H_2O)_4]$	**7**	**16**	**18**	**12**
$[(CoL)_2(H_2O)_4]$	**9**	**15**	**21**	**20**
$_2(L)(H_2O)_4]$) [(NiCl	**15**	**6**	**14**	**17**
$[(NiL)_2(H_2O)_4]$	**11**	**10**	**10**	**14**
$_2(L)(H_2O)_4]$)[(MnCl	**8**	**14**	**5**	**15**
$[(MnL)_2(H_2O)_4]$	**13**	**19**	**8**	**19**
$_2(L)(H_2O)_4]$)[(CuCl	**17**	**11**	**7**	**12**
$[(CuL)_2(H_2O)_4]$	**6**	**4**	**9**	**14**
$[(HgCl)_2(L)(H_2O)_4]$	**10**	**3**	**11**	**9**
$[(HgL)_2(H_2O)_4]$	**7**	**6**	**2**	**12**

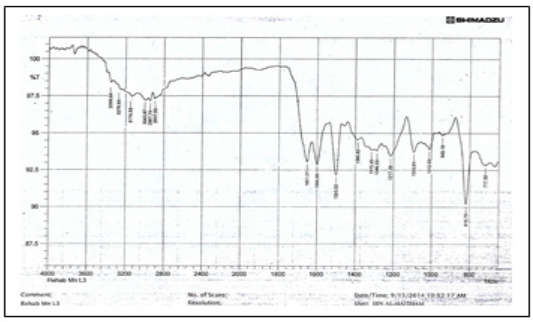
Fig(1) : The IR spectrum of the *Benzidine*



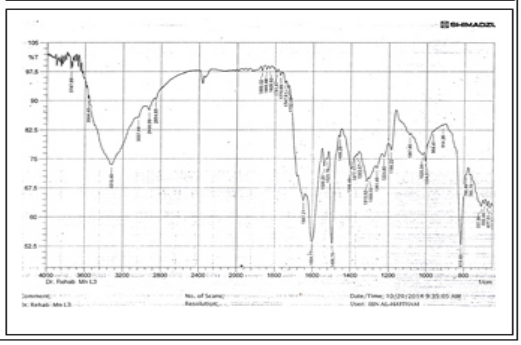
Fig(2) : The IR spectrum of the ligand(L)



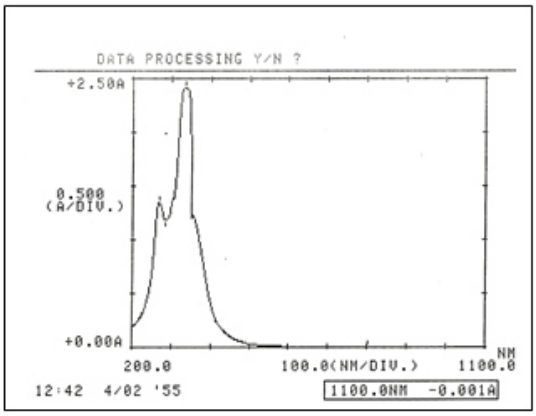
Fig(3) : The IR spectrum of $[(MnCl)_2(L)(H_2O)_2]$ complex



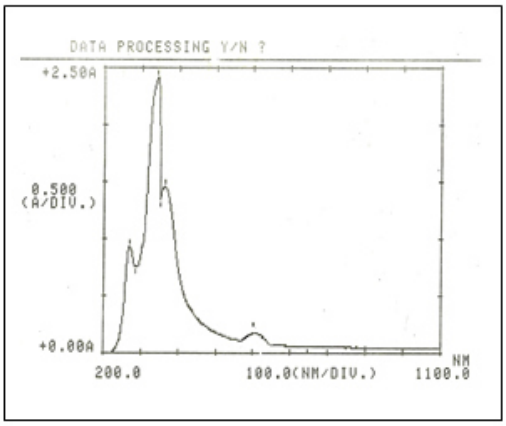
Fig(4) : The IR spectrum of $[(MnL)_2(H_2O)_4]$ complex



Fig(5): Electronic spectrum of the ligand(L)



Fig(6): Electronic spectrum of $[CoCl)_2(H_2O)_2]$complex



Fig(7): Electronic spectrum of $[(CoL)_2\{H_2O\}_4$complex

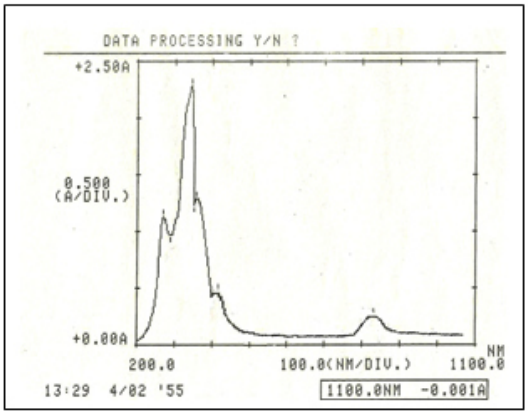


Fig.(8) *HNMR of Ligand*(L)

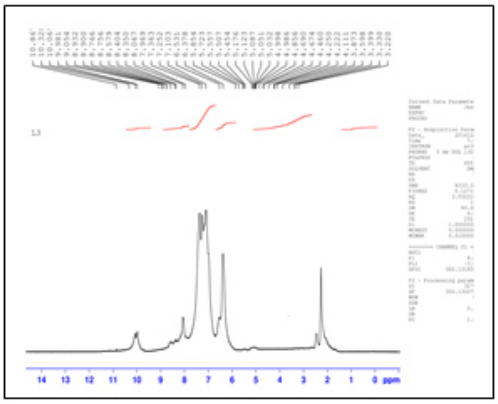


Fig.(9)^{13}C- *NMR of Ligand* (L)

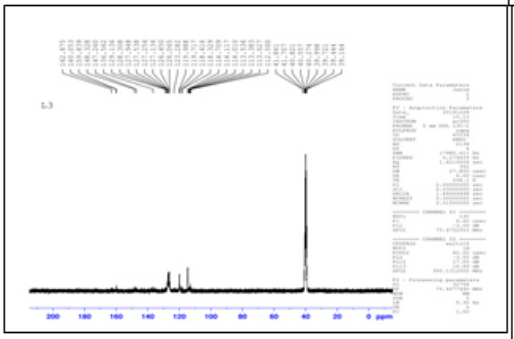
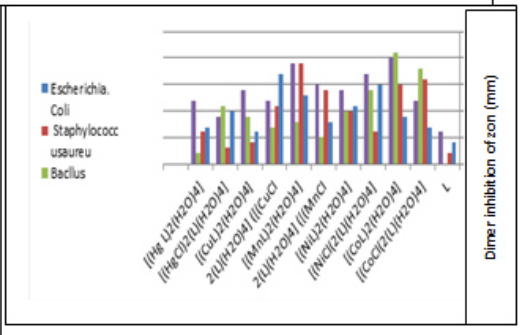


Fig.(9) Difference between the antimicrobial activity of binuclear ligand & metal complexes



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